The Effect Of Low Pressures of Ethylene on β-CUALCL$_4$

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Introduction: Copper aluminum tetrachloride is a catalyst and is used for separations of small molecules, as well as being a brilliant blue phosphor.[1] This halide structural analog to alumino-phosphates[2] occurs as two polymorphs, α and β, related by ccp and hcp anion sublattices, respectively.[3] Previous work at X7b demonstrated the reversible sorption of ethylene by α-$CuAlCl_4$ to yield one and two equivalent adducts.[4] In this communication we report the effect of low pressures of ethylene on β-$CuAlCl_4$ and the structural solution of the one equivalent adduct phase, $C_2H_4CuAlCl_4$.

Methods and Materials: β-$CuAlCl_4$ was loaded into capillaries then affixed to a goniometer/gas line to provide sample exposure of 10^{-2} to 10^3 Torr of ethylene. Time resolved X-ray diffraction data (TRXRD) were collected using the TIP camera and the MAR345. Single crystal data for $C_2H_4CuAlCl_4$ was extracted from the MAR345 image plates of a polycrystalline sample grown from the melt under a pressure of ethylene in an *ex situ* loaded capillary.

Results and Conclusions: The time resolved data for the exposure of β-$CuAlCl_4$ to 100 Torr of ethylene is shown in **Figure 1**. Upon exposure to ethylene the phase transition from β-$CuAlCl_4$ to α-$CuAlCl_4$ and incomplete formation of the ethylene adduct, $C_2H_4CuAlCl_4$, is observed. The small concentration of ethylene catalyzes the room temperature β to α phase transition, which, in the absence of ethylene, is only observed above about 100ºC as measured by ^{63}Cu MAS NMR and TRXRD.[5] In the thermally induced phase transition the rate of the transformation is correlated with the temperature of the melt from which samples of β-$CuAlCl_4$ were prepared; quenching from the higher temperature melt results in the higher rate constants. The faster rate is thought to correlate with a larger intrinsic defect concentration. By comparison, the ethylene catalyzed phase transition is likely a result of the creation of extrinsic defects.

$C_2H_4CuAlCl_4$ was found to crystallize in the space group $Pna2_1$, a=7.306, b=16.133, c=7.094. The structure, solved using SHELXS, exhibits one-dimensional chains of $C_2H_4CuAlCl_4$ that run parallel to the c axis (**Figure 2**). The links of these chains are made up of chloride-bridged four-rings of alternating Al and Cu with terminal coordination of an η^2-C_2H_4 ligand at Cu and a terminal chloride ligand at Al. The powder pattern calculated from this structure corresponds to the intermediate phase previously observed upon desorption of C_2H_4 from $(C_2H_4)_2CuAlCl_4$.[4]

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References: 1. Sullivan, R.M.; Martin J.D.; *J. Amer. Chem. Soc.* 1999, 121(43), 10092-10097. 2. Martin, J.D.; Dattelbaum, A.M.; Thornton, T.A.; Sullivan, R.M.; Yang, J.; Peachey, M.T. *Chem. Mat.* 1998, 10, 2699-2713. 3. Martin, J.D.; Leafblad, B.R.; Roger M. Sullivan, R.M.; Boyle, P.D. *Inorg. Chem.* 1998, *37*, 1341-1346. 4. Martin, J.D.; Sullivan, R.M.; Hanson, J.; Liu, H.; Ciraolo, M.F.; Grey, C.P. BNL National Synchrotron Light Source Activity Report, 1998, www.nsls.bnl.gov/Pubs/ActivR/AR-98/MA1218.pdf (accessed Sept. 1999). 5. Liu, H.; Sullivan, R.M.; Hanson, J.C.; Grey, C.P.; Martin, J.D., to be submitted.

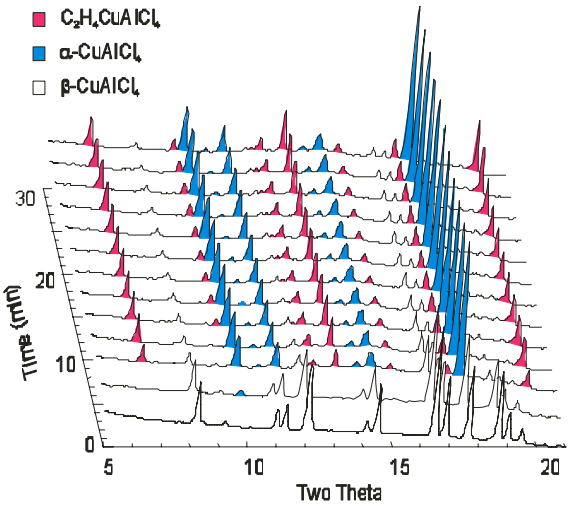

Figure 1. Variable atmosphere, time resolved powder X-ray diffraction. β-$CuAlCl_4$ was exposed to 100 Torr ethylene at t = 4 min.

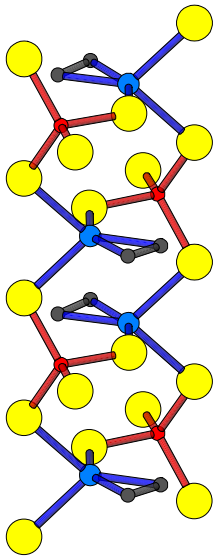

Figure 2. One-dimensional chain of $C_2H_4CuAlCl_4$.